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Abstract

Polysilanes with polyelectrolyte side chains are synthesized by two methods utilizing γ-ray-induced grafting and the pH responsiveness for one of those polymers is revealed mainly by investigating interfacial behavior of its monolayer at the air/water interface. In the first synthetic method, poly(methyl acrylate) is grafted onto poly(methyl-*n*-propylsilane) (PMPrS) through γ-ray-induced grafting, and then the PMA chains are hydrolyzed to poly(acrylic acid) in the yield of ca. 97%. Thus PMPrS with polyelectrolyte side chains is successfully synthesized by the graft chain hydrolysis.

The other method is the direct grafting of electrolyte monomers. Poly(methacrylic acid)-grafted PMPrS (PMPrS-*g*-PMAA) can be obtained through γ-ray-induced grafting of methacrylic acid monomers onto PMPrS chains, which shows the effectiveness of radiation grafting for the synthesis of polyelectrolyte graft copolymers. PMPrS-*g*-PMAA exhibits pH responsive behavior. In addition to the pH-dependence of water solubility, interfacial behavior also depends on the pH. Langmuir monolayers of PMPrS-*g*-PMAA exhibit different surface pressure-area isotherms according to the grafting yield and the pH of the subphase water. This result suggests that radiation modification is useful for fabricating polysilane-based ordered materials responsive to outer stimuli.

Keywords

Polysilanes / Graft Copolymers / γ-Rays / Radiation Modification / pH-Responsive polymer

1. Introduction

Polysilane has been receiving much attention due to its unique properties (Miller and Michl, 1989; West, 1986, 1992), and it is expected that nano-ordered polysilane-based materials exhibit further useful functionality. The utilization of self-assemblies is considered as a powerful method for preparing such ordered structures. Because of their capability for forming micelles and Langmuir films (Alexandridis and Lindman, 2000; Riess, 2003; Webber et al., 1996), amphiphilic block and graft copolymers are expected as promising candidate structures for nano-ordered polysilane-based materials.

Until now, we have been studying synthesis and characterization of polysilane-based

graft copolymers with amphiphilic chains such as poly(methyl methacrylate) (PMMA) and poly(diethyl fumarate) (PDEF) obtained through γ-ray-induced grafting of corresponding monomers (Tanaka et al., 2011). As a further development of these studies, we focused on stimuli-responsive polysilane-based graft copolymers with polyelectrolyte side chains. Ordered materials built up with this type of polymers are expected to be responsive to external stimuli such as pH and ionic strength, which attracts both industrial and scientific interest.

In this study, poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA) chains are grafted onto poly(methyl-*n*-propylsilane) (PMPrS) through γ-ray-induced graft polymerization. PAA-grafted PMPrS (PMPrS-*g*-PAA) was obtained by hydrolysis of poly(methyl acrylate) (PMA) graft chains of radiation-presynthesized PMA-grafted PMPrS (PMPrS-*g*-PMA), while PMAA-grafted PMPrS (PMPrS-*g*-PMAA) was directly synthesized with γ-ray-induced grafting of methacrylic acid (MAA) monomers onto PMPrS. To verify pH-responsiveness of ordered structures of these polysilane-based graft copolymers, surface pressure-area (π-A) isotherms of PMPrS-*g*-PMAA monolayers on the water subphase with different pH were examined.

2. Experimental

2.1. Synthesis

In series of our studies, PMPrS has been utilized as the trunk polymer for γ-ray induced grafting because PMPrS has good solubility in common organic solvents, the simplest side-chain structure among soluble polysilanes and relatively smaller molecular weight distribution (Miller and Michl, 1989). PMPrS was synthesized via the Wurtz-type coupling reaction of methyl-*n*-propyldichlorosilane. PMPrS was

purified by re-precipitation from a toluene solution into methanol, and then pure PMPrS was obtained by freeze-drying from a benzene solution. Number average molecular weight (M_n) and polydispersity index (PDI) were determined by GPC (RI detector) with polystyrene standards and a THF eluent. M_n and PDI of PMPrS used in the following experiments are listed in Table 1. PMPrS1 and PMPrS2 were employed for grafting PMA and PMAA, respectively.

Table 1. M_n and PDI of PMPrS used in the following experiments.

PMPrS-*g*-PMA and PMPrS-*g*-PMAA were synthesized in the following manner. PMPrS and purified each monomer were dissolved in toluene to given concentrations. The toluene solution in a glass tube was degassed, and then irradiated with ^{60}Co γ-rays at room temperature.

The toluene solution of PMPrS-*g*-PMA after γ-irradiation was poured into methanol to obtain a crude product. Because the product contained PMA homopolymer, it was purified by fractional precipitation with toluene/hexane. From the thin-layer chromatography (TLC) with toluene/methanol = 2/8 (v/v) eluent, the content of PMA homopolymer in PMPrS-*g*-PMA was confirmed to be less than 0.5 wt%.

PMPrS-*g*-PAA was prepared by hydrolysis of PMA graft chains of PMPrS-*g*-PMA. A sodium hydroxide aqueous solution containing 1.5 equivalents of hydroxide ions to an MA unit of the graft chains was added into a 1.0 wt% tetrahydrofuran (THF) solution of PMPrS-*g*-PMA. The solution was stirred at 60 °C for 5 h. After being cooled to room temperature, the solution was neutralized by adding hydrochloric acid and then the solvent was evaporated. NaCl salt contained in the crude product was removed by

solvent extraction of the graft copolymer with THF. The yield of hydrolysis was confirmed with ^{1}H NMR spectra. As the hydrolysis proceeds, the signal intensity at 3.65 ppm derived from methyl proton of PMA decreases. Accordingly, the yield was calculated from the intensity ratio of 3.65 ppm signals of PMPrS-*g*-PMA and PMPrS-*g*-PAA.

In the case of PMPrS-*g*-PMAA, the toluene solution after γ-irradiation was poured into a large amount of toluene to precipitate PMAA homopolymer. To remove residual PMAA homopolymer, a toluene solution of the product was centrifuged repeatedly. The content of PMAA homopolymer in the final product was confirmed by TLC to be less than 2.0 wt%.

The exact structures of the radiation-modified PMPrS could not be determined experimentally because reactive sites on PMPrS main chains are not limited to specific sites (Tanaka et al., 2011). However, the structures of radiation-modified PMPrS can be estimated by reference to other studies on radiation chemistry of polysilane. Seki et al. (1996) demonstrated by ESR study with poly(dimethylsilane) that radicals are generated on silicon atoms by elimination of methyl substituents upon γ-irradiation. Kumagai et al. (1996) clarified with poly(diethylsilane) and poly(cyclohexylmethylsilane) that radicals are generated on the alkyl side chains by homolytic cleavage of C-H bonds. In both cases, the initial process caused by γ-irradiation is the formation of radicals at an alkyl side-chain position. Since PMPrS has longer alkyl side chains than poly(dimethylsilane), Kumagai's case is more safely applicable to our case. As a result, it is considered that graft chains of the radiation-modified PMPrS are mainly bonded on alky side chains of PMPrS.

2.2. Spectroscopy

^{1}H NMR spectra were recorded on a JEOL EX 400 spectrometer at 25 ºC in deuterated chloroform solutions. UV absorption spectra were recorded on a Hitachi U-3400 spectrophotometer at room temperature. IR spectra were obtained with a PERKIN-ELMER 1800 by the KBr pellet method at room temperature.

2.3. Grafting yield

Grafting yield is defined as the number of each monomer units per silicon atom of PMPrS. Grafting yield of PMPrS-*g*-PMA was determined from the integrated intensity ratio of ^{1}H NMR signals (methyl proton of PMA ($COOCH_3$, δ 3.65 ppm) to methyl proton of PMPrS ($SiCH_3$, δ 0.25 ppm)).

Grafting yield of PMPrS-*g*-PMAA was estimated from the UV absorption spectra of its THF solution. The molar absorption coefficient of PMPrS is not changed by γ-irradiation as described in the following section. Therefore, the molar absorption coefficient of PMPrS-*g*-PMAA (ε) is expressed by $\varepsilon = \varepsilon_0 / (1 + M_r f)$, where ε_0 is the molar absorption coefficient of PMPrS homopolymer, M_r the ratio of molecular weight of a MAA unit to that of a methyl-*n*-propylsilane unit, and f grafting yield. If the concentration of PMPrS homopolymer and PMPrS-*g*-PMAA solutions is the same, ε and ε_0 in the above equation are replaced by the corresponding absorption intensity A and A_0. Thereby grafting yield f is evaluated by $f = (A_0 / A - 1) / M_r$.

2.4. π-A isotherm

Benzene solutions of 0.1 g/L of PMPrS-*g*-PMAA were spread at 20 °C on the

subphase water, which was previously purified by deionization with a Millipore filtration system followed by distillation and then pH-adjusted by adding hydrochloric acid or sodium hydroxide aqueous solutions. The monolayers at the air/water interface were compressed at a speed of 20 cm^2/min and the π-A isotherms were monitored with a Wilhelmy plate.

3. Results and Discussion

3.1. Synthesis of PMPrS-*g*-PAA

Firstly we tried to hydrolyze PMMA chains of PMMA-grafted PMPrS (PMPrS-*g*-PMMA) obtained in our previous study (Tanaka et al., 2011), but the result was less than satisfactory. Thus we planned to presynthesize the PMPrS-based graft copolymer whose graft chains have higher reactivity in hydrolysis. PMA was selected as such graft chains because it is more susceptible to hydrolysis due to lack of α-methyl groups exerting inductive effects. Figure 1 shows the dependence of grafting yield of PMPrS-*g*-PMA on total absorption dose. Grafting yield increases as dose rises, which indicates that grafting yield of PMPrS-*g*-PMA can be controlled by changing dose.

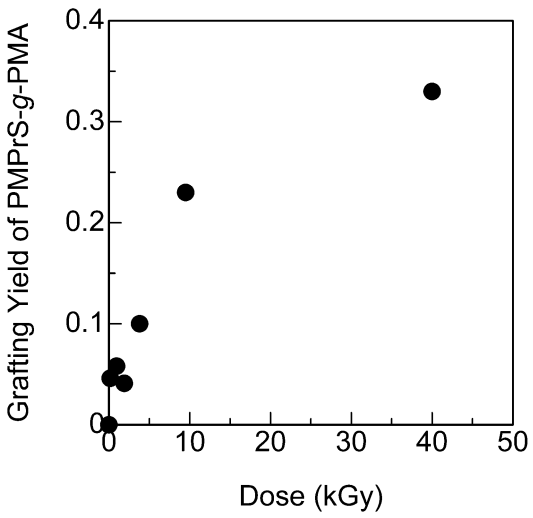

Figure 1. Dependence of grafting yield of PMPrS-*g*-PMA on dose. The concentrations of PMPrS and MA were 10 and 20 wt%, respectively.

A graft density of PMPrS-*g*-PMA can be estimated by referring to our previous study on PMPrS-*g*-PMMA (Tanaka et al., 2011). PMPrS-*g*-PMMA has a low graft density, and the number of PMMA graft chains per PMPrS main chain is estimated to be less than 1.0. Such a low graft density is explained by the high propagation rate constant of methyl methacrylate (MMA). Since methyl acrylate (MA) has the higher propagation rate constant than MMA, it is supposed that PMPrS-*g*-PMA also has a low graft density and the number of PMA graft chains per PMPrS main chain is less than 1.0.

Polysilanes have generally larger *G* values for scission, *G*(s), than those for cross-linking, *G*(x), upon γ-irradiation, which indicates that polysilanes predominantly undergo chain scission by γ-rays (Miller and Michl, 1989). For example, *G*(s) and

G(x) values of poly(di-*n*-butylsilane) which has the similar structure to PMPrS are 0.42 and 0.023, respectively. Although aryl-substituted polysilanes have relatively higher *G*(x) values than alkyl-substituted polysilanes due to the protecting effect by aryl groups, still the chains of aryl-substituted polysilanes are also degraded by γ-rays (Seki et al., 1998). We also confirmed that PMPrS is degraded by γ-irradiation (Tanaka et al., 2011). Accordingly, it was verified that PMPrS-*g*-PMA keeps the electronic property of PMPrS even after γ-irradiation. As shown in Figure 2, UV absorption spectra of PMPrS and PMPrS-*g*-PMA are scarcely different. The molar absorption coefficient neither changes by irradiation. This result indicates that the electronic property derived from the delocalized electrons along the silicon backbone is scarcely affected by the radiation-modification.

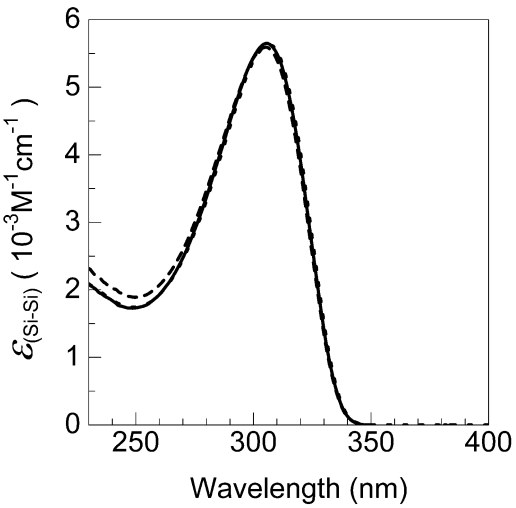

Figure 2. UV absorption spectra of THF solutions of PMPrS (dotted line), PMPrS-*g*-PMA (broken line) and PMPrS-*g*-PAA (solid line) with grafting yield of 0.33.

Next, PMA chains of PMPrS-*g*-PMA were hydrolyzed to PAA chains in the manner described in the experimental section. The yield of the hydrolysis was ca. 97%. Since sodium hydroxide is strong base, there is some possibility that PMPrS main chains are also hydrolyzed and its electronic property is changed. As seen in Figure 2, however, the spectral profile and the molar absorption coefficient of PMPrS-*g*-PAA are almost the same as those of PMPrS homopolymer, which shows that the electronic property of PMPrS main chains is not changed by hydrolysis. Thus, PMPrS-*g*-PAA was successfully synthesized by hydrolysis of grafted PMA chains.

3.2. Synthesis of PMPrS-*g*-PMAA

The preparation method described in the previous section includes two reaction steps. As a simpler method to prepare similar polysilane, we tried direct synthesis of polysilane with polyelectrolyte side chains.

Figure 3 shows IR spectra of PMPrS-*g*-PMAA irradiated with different doses. The absorption peaks at 1120, 1280, and 1700 cm^{-1} derived from carboxyl groups of PMAA chains increase with rising dose. This result demonstrates that PMAA chains are successfully grafted onto PMPrS chains through γ-ray-induced grafting of MAA monomers.

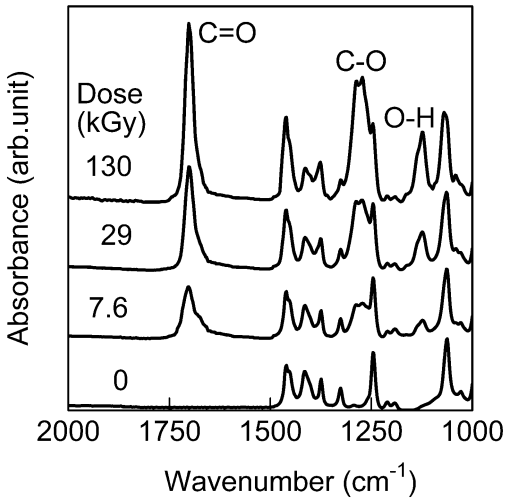

Figure 3. IR spectra of PMPrS-*g*-PMAA irradiated with different doses. Dose rate was 1.9 kGy/h. The concentrations of PMPrS and MAA were 10 and 20 wt%, respectively.

Figure 4a shows the dependence of grafting yield of PMPrS-*g*-PMAA on dose. Grafting yield increases with rising dose. This tendency is consistent with the case of PMPrS-*g*-PMMA (Tanaka et al., 2011). However, grafting yield of PMPrS-*g*-PMAA is lower than that of PMPrS-*g*-PMMA at the similar doses. Because PMAA chains is almost insoluble in toluene, solutions of PMPrS-*g*-PMAA become gel-like by γ-irradiation and the fluidity of the PMPrS-*g*-PMAA solutions declines. Consequently, the efficiency of the radical reaction in the PMPrS-*g*-PMAA solutions lowers compared to that in PMPrS-*g*-PMMA solutions, and grafting yield of PMPrS-*g*-PMAA becomes lower than that of PMPrS-*g*-PMMA.

The same phenomenon appears in the dependence of grafting yield of PMPrS-*g*-PMAA on dose rate. Grafting yield decreases with rising dose rate in Figure

4b. This tendency is also consistent with the case of PMPrS-*g*-PMMA, but grafting yield of PMPrS-*g*-PMAA is lower than that of PMPrS-*g*-PMMA at the similar dose rates.

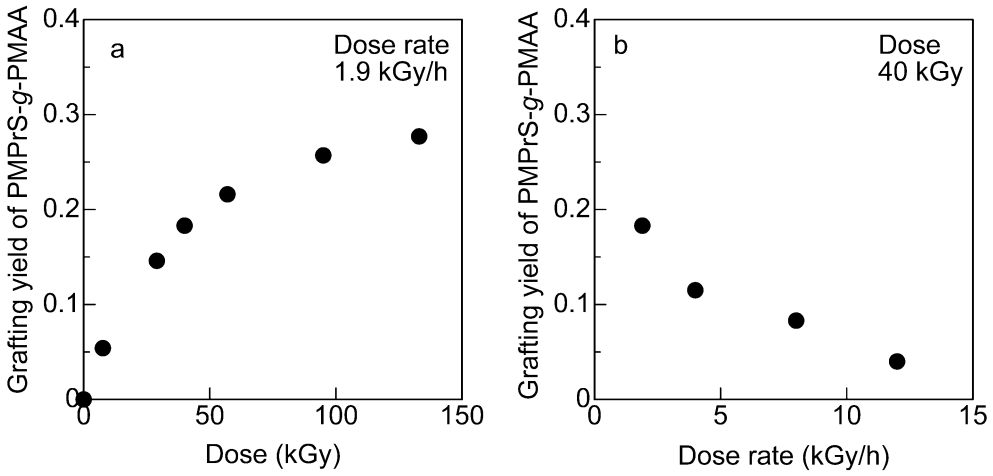

Figure 4. Dependence of grafting yield of PMPrS-*g*-PMAA on (a) dose and (b) dose rate. The concentrations of PMPrS and MAA were 10 and 20 wt%, respectively.

Figure 5 depicts the dependence of grafting yield of PMPrS-*g*-PMAA on the concentration of MAA. Grafting yield increases in the range from 0 to 20 wt%. However, the change of grafting yield is scarcely recognized in the range from 20 to 30 wt%, and finally the grafting yield decreases at 40 wt%. At higher MAA concentrations, solutions of PMPrS-*g*-PMAA become solid by γ-irradiation. Diffusion of MAA monomers to PMPrS chains is reduced in the radical reaction, which results in the decrease of grafting yield at high MAA concentrations.

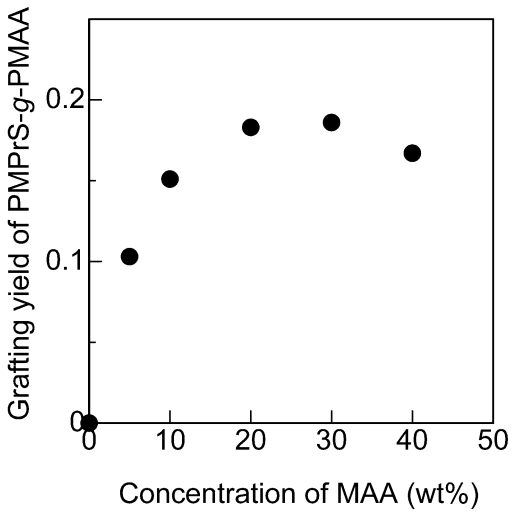

Figure 5. Dependence of grafting yield of PMPrS-*g*-PMAA on the concentration of MAA. The concentration of PMPrS was 10 wt%. Dose rate was 1.9 kGy/h and dose was 40 kGy.

PMPrS-*g*-PMAA indicates different solubility to water depending on its pH. PMPrS-*g*-PMAA is soluble in neutral and alkaline water, but not in acidic water. In addition, PMPrS-*g*-PMAA dissolved in the neutral water forms emulsion, while that in the alkaline water gives a transparent solution. This fact indicates that PMPrS-*g*-PMAA shows better solubility in higher-pH water, which corresponds to the characteristics of PMAA. The result obtained here demonstrates that PMPrS becomes responsive to ambient pH condition due to introduction of PMAA graft chains.

3.3. π-A isotherms of PMPrS-*g*-PMAA

The interfacial behavior of PMPrS-*g*-PMAA was investigated by π-A isotherm measurements. Figure 6 displays π-A isotherms of PMPrS-*g*-PMAA monolayers at the

air/water interface. The π-A isotherm of polysilane homopolymer exhibits a condensed profile because hydrophobic PMPrS cannot spread over the water surface. On the other hand, the π-A isotherms of PMPrS-*g*-PMAA show expanded profiles, and the limiting area of the PMPrS-*g*-PMAA monolayer increases with rising grafting yield.

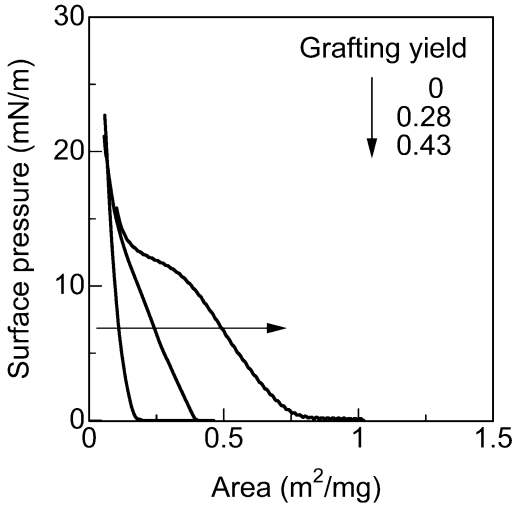

Figure 6. π-A isotherms of PMPrS-*g*-PMAA monolayers at the air/water interface. The pH of the water subphase is 7.

Next, we investigated π-A isotherms of PMPrS-*g*-PMAA monolayers on the water of different pH values to verify the pH-responsiveness of PMPrS-*g*-PMAA. Figure 7a and 7b display π-A isotherms of PMPrS-*g*-PMAA with different grafting yield. In Figure 7a, the limiting area increases with rising pH. At pH = 7 and 12, PMAA graft chains are negatively charged because pK_a of PMAA is 5.65 and the carboxyl groups of PMAA graft chains release protons (Greenwald and Luskin, 1980). Under such conditions, PMAA graft chains repel each other on the water subphase due to the negative charge. On the other hand, PMAA graft chains are not charged at pH = 2

because the carboxyl groups are protonated. Consequently, the π-A isotherms at pH = 7 and 12 show more expanded profiles than that at pH = 2. The number of negatively charged MAA units and the repulsive force among PMAA chains become larger at pH = 12 than at pH = 7. As a result, the limiting area increases in this order.

Figure 7b displays π-A isotherms of PMPrS-*g*-PMAA with higher grafting yield. The π-A isotherm at each pH shows more expanded profile than that in Figure 7a. However, the limiting area in Figure 7b decreases with rising pH contrary to that in Figure 7a. The water solubility of the graft polymer is responsible for this result. PMPrS-*g*-PMAA with higher grafting yield is more soluble in neutral and alkaline water than that with lower grafting yield. The solubility of PMPrS-*g*-PMAA to alkaline water is higher than that to neutral one. As the monolayers are compressed to a smaller surface area, some of the polymer lying on the water surface dissolve into the water. Accordingly, the limiting area at pH = 12 becomes smaller than that at pH = 7. In contrast, PMPrS-*g*-PMAA does not dissolve in acidic water. As a result, the π-A isotherm at pH = 2 exhibits more expanded profile than those at pH = 7 and 12.

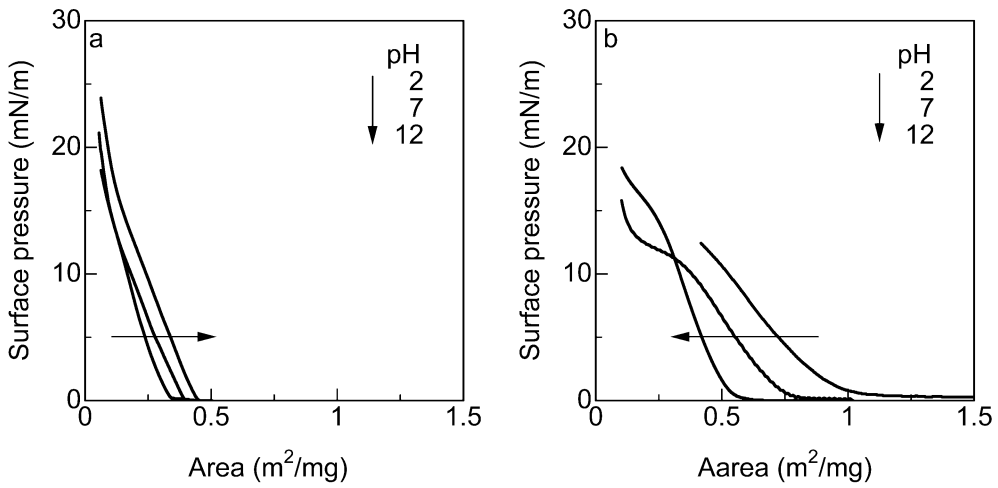

Figure 7. π-A isotherms of PMPrS-*g*-PMAA with grafting yield of (a) 0.28 and (b) 0.43 on the water of different pH values.

4. Conclusion

Polysilanes with polyelectrolyte graft chains were successfully obtained by two different methods: one is the hydrolysis of graft chains of a polysilane-based graft copolymer presynthesized through γ-ray-induced grafting, and the other is the direct grafting of electrolyte monomers onto polysilane chains by γ-irradiation. In the first method, the hydrolysis yield of graft-chain ester units of PMPrS-*g*-PMA was found to be ca. 97%, which proves that this method is useful for obtaining polysilane with polyelectrolyte graft chains, PMPrS-*g*-PAA. In the second method, PMPrS-*g*-PMAA was directly synthesized through γ-ray-induced grafting of MAA monomers onto PMPrS chains. It was thus shown that γ-ray-induced grafting is useful to give polysilane with polyelectrolyte graft chains. By utilizing PMPrS-*g*-PMAA obtained by the second method, it was observed that polysilane with polyelectrolyte graft chains shows pH responsive behaviors. As an instant result of this, the solubility in water becomes dependent on its pH. PMPrS-*g*-PMAA is soluble in neutral and alkaline water, but not in acidic water. Interfacial behavior is also pH-dependent. Limiting areas of PMPrS-*g*-PMAA monolayers with lower grafting yield increase with rising pH due to the repulsive force among negatively charged PMAA chains. On the other hand, limiting areas of PMPrS-*g*-PMAA monolayers with higher grafting yield decrease with rising pH due to the water solubility of the graft polymer. These results demonstrate that the fabrication of ordered materials responsive to outer stimuli is feasible by utilization of radiation-modified polysilane with polyelectrolyte side chains.

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Figure Captions